Suppression of Hydrogen Embrittlement in Stainless Steel by Surface Modification

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論 文 内 容 要 旨

Chapter 1　Introduction

The objective of this study is to construct a method for suppression of hydrogen embrittlement in stainless steel by surface modification employing cavitation peening. Hydrogen is attractive energy carrier without any greenhouse gas during the usage of it. The society based on hydrogen energy is called as hydrogen society. Metallic materials are indispensable in an infrastructure for hydrogen society now and in the future. However, there is an important problem so-called "hydrogen embrittlement". Hydrogen easily invades the metallic materials and reduces mechanical properties: ductility, tensile toughness and fatigue strength. Namely, hydrogen makes the metallic materials brittle, and accelerates crack growth. To use hydrogen safely, a method for suppression of hydrogen embrittlement needs to be constructed. From past reports, it was revealed that hydrogen has a tendency to concentrate elastic-plastic boundary around a crack tip where hydrostatic stress has a maximum value. Since the hydrostatic stress largely affects hydrogen diffusion and concentration behavior in metallic materials, peening which is one of the surface modification techniques can be applied to suppress hydrogen embrittlement in view point of reduction of the hydrostatic stress due to the introduction of compressive residual stress.

Chapter 2　Suppression of Fatigue Crack Growth with Hydrogen Embrittlement at Crack Initiation Stage in Austenitic Stainless Steel by Cavitation Peening

In order to verify the effect of cavitation peening on the fatigue crack growth in hydrogen-charged SUS316L, the fatigue crack growth test was conducted by a plate bending fatigue tester with the applied stress of 350 MPa after cathodic hydrogen charging with and without treatment by cavitation peening employing a cavitating jet in water with one treatment condition. Hydrogen charging was done during 96 hours. Hydrogen accelerated the fatigue crack growth at crack initiation stage and this acceleration of crack growth was not caused in treated surface. The fatigue crack growth rate was reduced by 66 % by cavitation peening.

Chapter 3 Suppression of Fatigue Crack Growth with Hydrogen Embrittlement in Austenitic Stainless Steel by Cavitation Peening

In Chapter 3, the fatigue crack growth in SUS316L after 168 hours hydrogen charging was conducted. Firstly, the fatigue crack growth test in untreated specimen was done with three applied bending stress of 300, 350 and 400 MPa. Figure 3-5 plots the fatigue crack length, $2a$, as a function of the number of cycles, N, for various applied bending stress, σ_a. Surprisingly, hydrogen-assisted crack growth was remarkably observed at the applied stress of 300 MPa differently from those of 350 and 400 MPa, as shown in Fig. 3-5. Some sub-crack was caused around a main-crack propagated from the pre-crack and then those sub-cracks were coalesced with the main-crack. This phenomenon rapidly accelerated the crack growth and caused an expected fracture unlike the cases with the applied stress of 350 and 400 MPa. The acceleration induced by hydrogen charging was not observed in specimens treated by cavitation peening employing a cavitating jet in air regardless of its processing time. Figure 3-10 plots the fatigue crack length as a function of the number of cycles for the processing time of 0 (Not-treated), 0.25 and 20 s/mm with and without hydrogen charging. It indicates a short treatment can be effective for suppression of hydrogen-assisted crack growth. The fatigue life of hydrogen charged specimen was same as that of uncharged specimen. The number of cycles to failure and the crack growth rate with hydrogen charging were increased by almost a factor of 3 and reduced by 75 %, respectively, compared to an untreated sample.

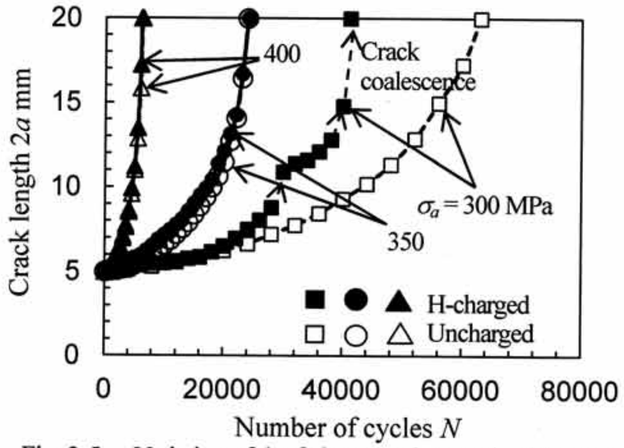

Fig. 3-5 Variation of the fatigue crack growth with applied bending stress after hydrogen charging

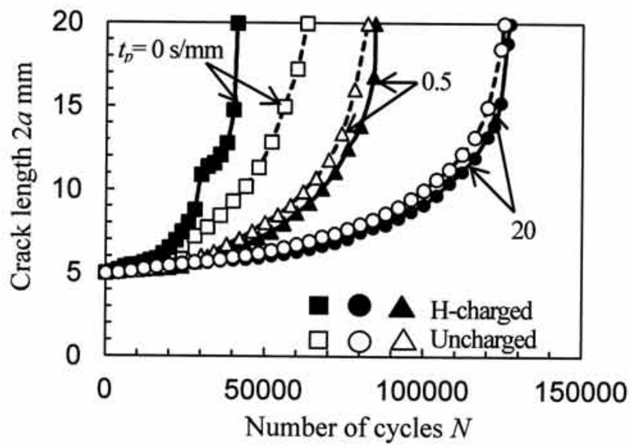

Fig. 3-10 Suppression of hydrogen-assisted fatigue crack growth by cavitation peening

Chapter 4 Numerical Simulation of the Effect of Residual stress on the Concentration of Hydrogen around a Crack Tip

By a numerical simulation using finite element analysis, the effect of residual stress on the concentration of hydrogen around a crack tip on a plastic deformed field generated by a fatigue process in austenitic stainless steel (SUS316L) was investigated. The residual stress was varied from -500 MPa (compressive) to 500 MPa (tensile) every

50 MPa. Figure 4-3 plots the normalized hydrogen concentration, C/C_0, as a function of depth from the crack tip, d_t, for various residual stress, σ_R. The hydrogen concentration around the crack tip was increased along with increasing the residual stress. Namely, tensile residual stress increased it and compressive residual stress reduced it. It is because that residual stress largely affects the hydrostatic stress around the crack tip, i.e., crack closure or opening effect. As a result, compressive residual stress reduced the concentration of hydrogen due to the crack closure effect. The results show peening can be effective to increase the resistance of SUS316L to hydrogen embrittlement.

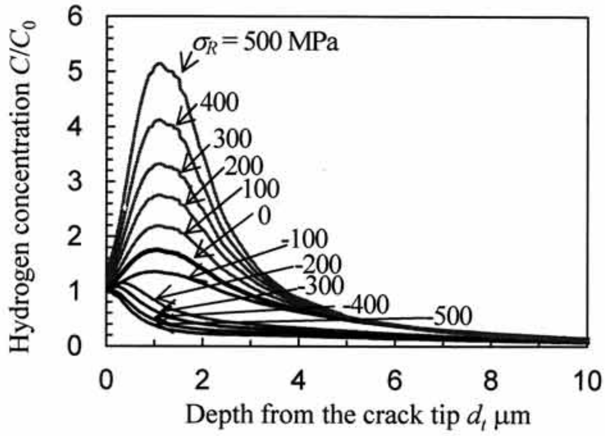

Fig. 4-3 Hydrogen concentration behavior around the crack tip for various residual stress

Chapter 5 Effect of Cavitation Peening on the Hydrogen-Induced Surface Hardening of Austenitic Stainless Steel Evaluated by Indentation Test

In Chapter 5, the effect of hydrogen on surface hardening was verified by indentation tests using a spherical indenter, in order to demonstrate that compressive residual stress can suppress hydrogen invasion into the surface of SUS316L through the evaluation of hydrogen-induced surface hardening. The tests were conducted on SUS316L treated by cavitation peening with varying the hydrogen charging time employing the cathodic hydrogen charging. The surface hardening induced by hydrogen was evaluated by indentation test using a spherical indenter whose diameter was 100 μm. Figure 5-6 plots the rate of change with the maximum indentation depth before and after 48 hours hydrogen charging normalized by the value before hydrogen charging, $\Delta h_{d\,max}/h_{d\,max0}$, as a function of the compressive residual stress introduced by cavitation peening, σ_{cR}. The surface hardened with increasing hydrogen charging time and by nearly 35 % after 48 hours hydrogen charging in the not-treated specimen. In the case of the treated specimen by cavitation peening, the surface hardening rate decreased with increasing compressive residual stress as shown in Fig. 5-6. Moreover, when large compressive residual stress was introduced at the surface, the rate shown in Fig. 5-6 was nearly 0, i.e., hydrogen-induced surface hardening did

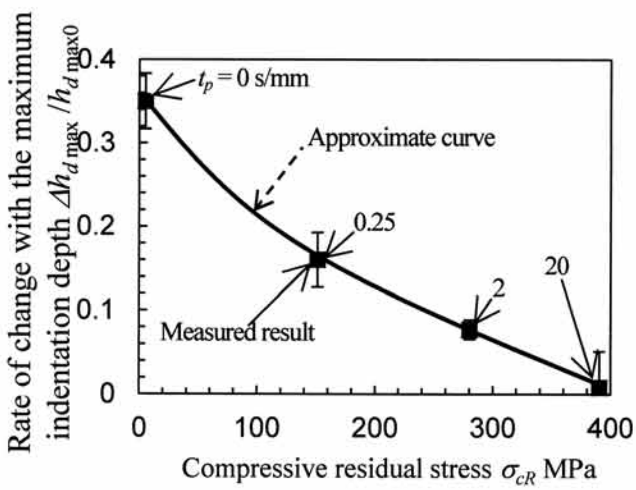

Fig. 5-6 Suppression of hydrogen-induced surface hardening by introduction of compressive residual stress

not occur. It can be concluded that peening can be an effective technique to suppress not only the concentration of hydrogen around a crack tip but also hydrogen invasion into the surface.

Chapter 6 Estimation of the Depth of Surface Modification Layer Treated by Cavitation Peening

A straight-forward method for evaluating the modified layer depth treated by cavitation peening was proposed. This method needs to measure the curvature and surface residual stress caused by cavitation peening and calculate based on beam theory in order to obtain the modified layer depth. For practical application, the depth of modified layer can be estimated by following steps: (1) Preparation of the specimen made of same material for the components or structures. (2) Treatment of the specimen by cavitation peening in the same condition. One specimen will be enough. Several specimens at various thickness would be better to obtain accurate result. (3) Measurement of the radius of curvature and the surface residual stress (4) Calculation of the depth of modified layer based on beam theory (5) Calculation of the depth of introduced compressive residual stress.

Chapter 7 Optimizing the Pitch of Scanning Nozzle for a Cavitating Jet on Overlapping Treatment during Peening

The pitch of scanning nozzle of cavitating jet for cavitation peening on overlapping treatment during peening was optimized in order to treat effectively and uniformly by employing a cavitating jet. The aggressive intensity distribution of the jet was estimated based on a Gaussian distribution in consideration of the probability distribution of cavitation bubbles collapsing. The treatment was done with various pitches of scanning nozzle on the aluminum surface. When the surface was treated with the pitch of not less 6 mm, some stripe patterns due to the non-uniform treatment was observed differently from those of 2 and 4 mm. In view point of the introduction of compressive residual stress, it can be introduced about 380 and 400 MPa with the pitch of 4 and 2 mm, respectively. In consideration of not only the uniform treatment but also effective treatment, the pitch of 4 mm would be better than that of 2 mm since twice the number of treatment time is needed to increase compressive residual stress by 10 % in the case of the pitch of 2 mm compared to that of 4 mm.

Chapter 8 Conclusions

In order to demonstrate the suppression of hydrogen embrittlement caused in stainless steel by a surface modification, cavitation peening was employed as the surface modification technique in this study. It was demonstrated that hydrogen-assisted fatigue crack growth in stainless steel can be suppressed by compressive residual stress introduced by cavitation peening. The compressive residual stress has an important role to reduce the concentration of hydrogen around a crack tip and to suppress the invasion of hydrogen from the surface. Thus, peening can be an effective technique for not only enhancing the mechanical property of metals but also for increasing their resistance to hydrogen embrittlement. In Chapters 6 and 7, methods to evaluate the depth of compressive residual stress and to optimize the pitch of cavitation peening for uniform treatment were proposed, respectively.

論文審査結果の要旨

環境負荷低減の観点から水素燃料を基盤とした水素社会の実現が望まれているが、金属材料を水素環境で使用すると静的強度や疲労強度が低下する水素脆化が一つの障壁となっている。本研究では、引張応力が水素脆化を促進する事実に注目し、金属材料に圧縮残留応力を付与する表面改質により水素脆化を抑止する方法を提案し、水素環境下での使用が想定されているオーステナイト系ステンレス鋼SUS316L を取り上げ、表面改質による水素脆化抑止を実証するとともに、圧縮残留応力による水素侵入の抑止効果を水素拡散凝集解析により検証し、表面改質による水素脆化抑止法の基礎を構築している。本論文は、これらの研究成果をまとめたものであり、全編8章からなる。

第1章は序論であり、本研究の背景、目的および構成を述べている。

第2章では、表面改質としてキャビテーション気泡の崩壊衝撃力により圧縮残留応力を導入するキャビテーションピーニングを取り上げ、表面処理材と未処理材を水素環境にさらした後で予亀裂を付与して平面曲げ式疲労試験に供し、亀裂進展初期における表面改質による水素脆化抑止を実験的に実証するとともに、その基礎となる供試材の水素チャージ法ならびに表面改質層の亀裂進展評価法を提案している。これらは、本研究の基盤となる成果である。

第3章では、疲労強度近傍において水素脆化が顕著になることと、表面改質により亀裂進展速度を 1/3 程度に低減できることを明らかにしている。これらは、表面改質による水素脆化の顕著な抑止効果を実証した貴重な成果である。

第4章では、有限要素法を用いた水素拡散凝集解析を行い、圧縮残留応力導入による水素侵入の抑止効果を検証している。これは、表面改質による水素脆化抑止機構解明の観点から重要な成果である。

第5章では、水素環境にさらすとステンレス鋼の微小押込み硬さが増大する事実を見出したことに基づき、微小押込み試験による水素侵入の簡易的評価手法を提案して表面改質による水素侵入抑止を実証している。これは、材料の水素脆化敏感性の簡易評価手法として有用な知見である。

第6章では、表面改質による圧縮残留応力が水素脆化抑止の支配因子であることを踏まえて、表面改質した板材に生じる反りから圧縮残留応力が導入される深さを簡易的に評価する手法を提案して検証している。これは、表面改質を施工する際に工業的に有用な成果である。

第7章では、キャビテーションピーニングにおいて、一様に圧縮残留応力を導入するためのキャビテーション噴流の最適な走査間隔の同定法を提案して検証している。これは、実用上有益な成果である。

第8章は結論である。

以上要するに本論文は、表面改質層の評価手法を構築した上で、水素脆化を抑止する表面改質を提案、検証し、表面改質による水素脆化抑止法の基礎を開拓したものであり、ナノメカニクスおよび機械工学の発展に寄与するところが少なくない。

よって、本論文は博士(工学)の学位論文として合格と認める。